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# The Chemistry on Diterpenoids in 1977. Part-I

AUTHOR(S):

Fujita, Eiichi; Fuji, Kaoru; Nagao, Yoshimitsu; Node, Manabu

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Review

## The Chemistry on Diterpenoids in 1977. Part-I

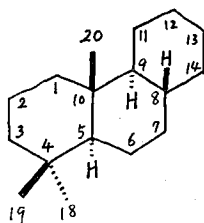
Eiichi FUJITA,\* Kaoru FUJI, Yoshimitsu NAGAO, and Manabu NODE

Received May 23, 1978

### I. INTRODUCTION

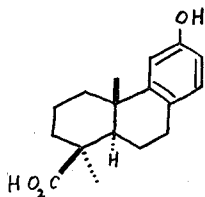
This is one of a series of our annual reviews<sup>1)</sup> on diterpenoids chemistry. The classification of the compounds is the same as that adopted in our reviews since 1969. This review covers the literatures published between January and June 1977.

### II. PODOCARPANE DERIVATIVES

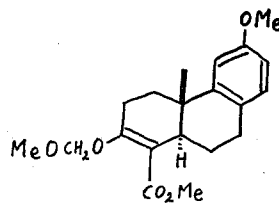


Podocarpane

Stereoselective total synthesis of *rac*-podocarpic acid (1) was published.<sup>2)</sup> Key step of the synthesis consists of concomitant reduction, deoxygenation, and stereoselective alkylation of vinyl ester 2 by treatment with lithium metal in liquid ammonia and dimethoxyethane followed by methyl iodide. This method provides a general synthetic procedure for the construction of podocarpane type natural products.



(1)



(2)

Baeyer-Villiger oxidation of 7-oxo compounds 3 and 4 and ring-B cleavage followed

\* 藤田栄一, 富士 薫, 長尾善光, 野出 学: Laboratory of Physiological Activity, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan.

by ring-B recyclization afforded 11, 14-dimethoxypodocarpic acid derivatives **5** and **6** respectively. The reaction sequence is outlined in Chart 1.<sup>3)</sup>

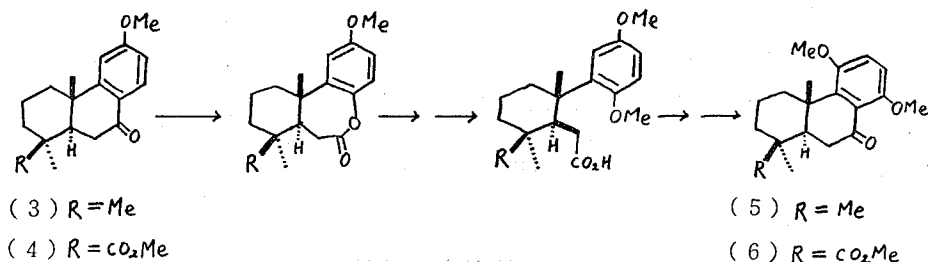
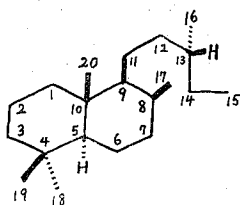


Chart 1

Rearrangement of the epoxide **7** with boron trifluoride etherate gave compound **8** in 32% yield.<sup>4)</sup> The synthesis of (–)-podocarpic acid from (+)-dehydroabietic acid was reviewed.<sup>5)</sup> Effects of 54 podocarpane derivatives on the growth of rice and barnyard grass seedlings were investigated.<sup>6)</sup>



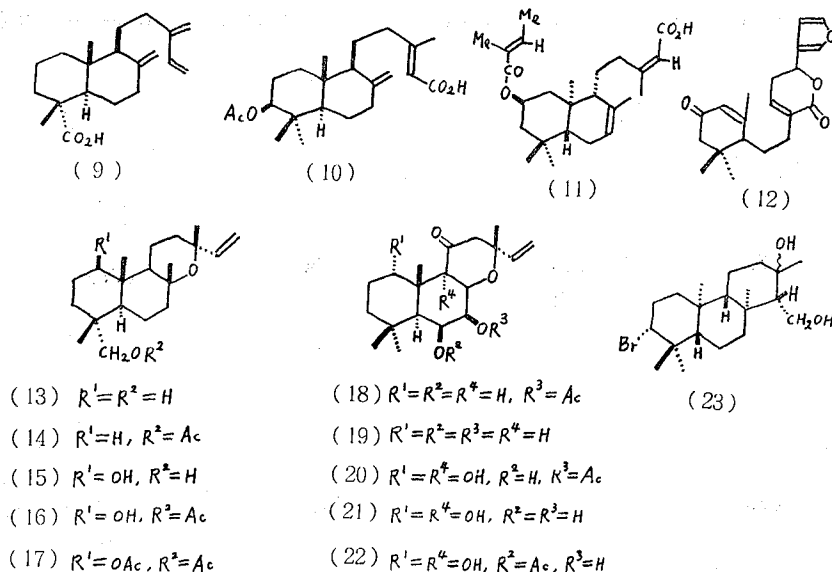
### III. LABDANE DERIVATIVES



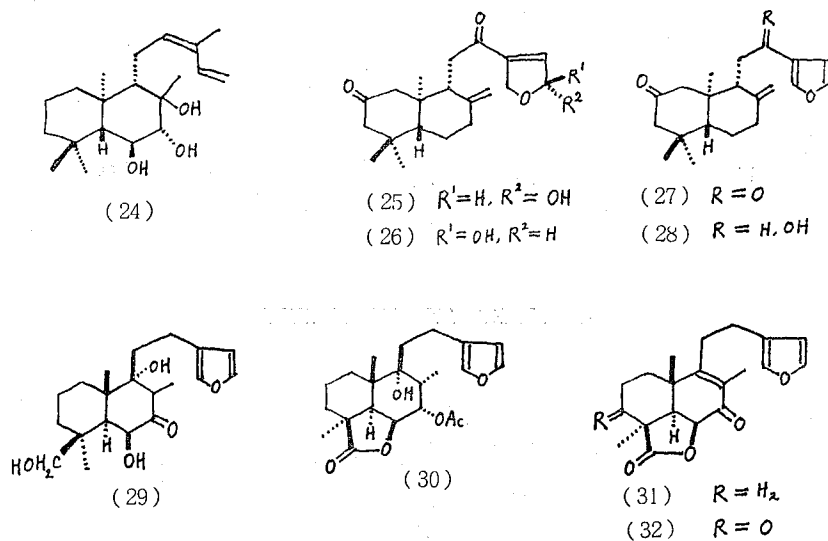
Labdane

A new diterpene, 4-epiisocommunic acid (**9**) was isolated as the methyl ester from *Callitris rhomboidea*.<sup>7)</sup> The structure **10** of a new diterpene isolated from *Metasequoia glyptostroides* was determined mainly by <sup>13</sup>C NMR spectroscopy.<sup>8)</sup> New diterpenes, dendroidinic acid (**11**) and hebeclinolide (**12**), were isolated from *Ageratina dendroides* and *Hebeclinium macrophyllum* respectively.<sup>9)</sup>

Five new labdane diterpene oxides, jhanol (**13**), jhanol acetate (**14**), jhanidiol (**15**), jhanidiol-18-monoacetate (**16**) and jhanidiol diacetate (**17**), were isolated from *Eupatorium jhanii*.<sup>10)</sup> *Coleus forskohlii* was found to contain five diterpenoids, **18–22**, three of which (**20–22**) display blood pressure lowering and cardioactive properties.<sup>11)</sup>



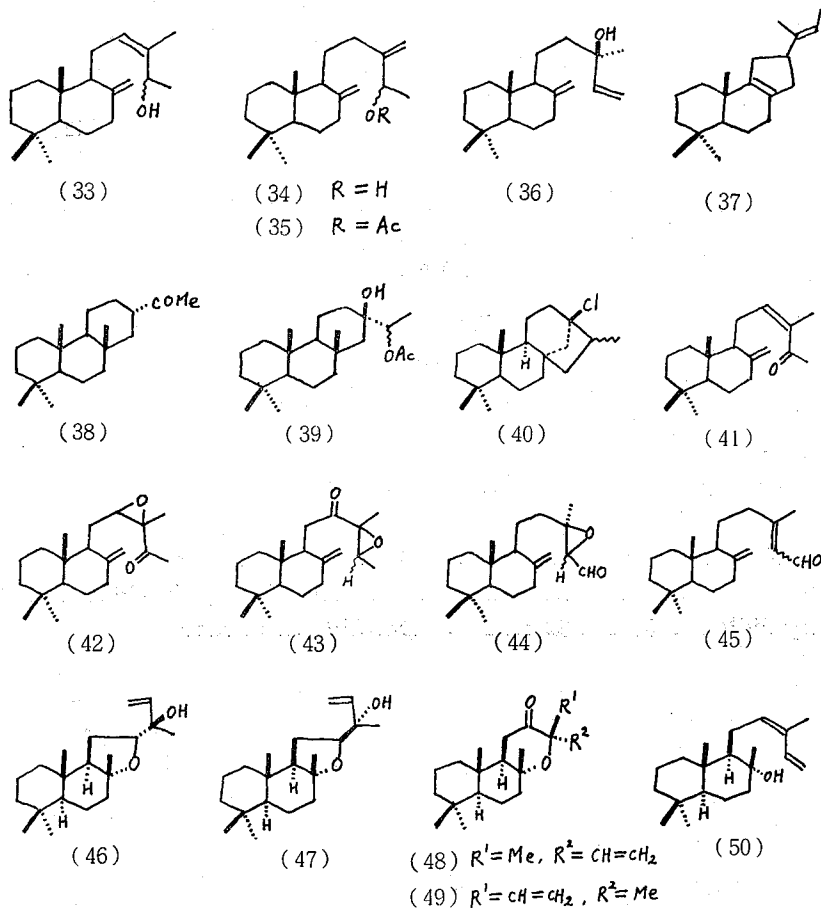
A brominated diterpene, isoapsin-20 (23) was isolated from a sea fish, *Aplysia kurodai*.<sup>12)</sup> New diterpenes 24-28 from *Austro eupatorium inulaefolium*,<sup>13)</sup> 29 and 30 from *Ballota nigra*<sup>14,15)</sup> and 31 and 32 from *B. rupestris*<sup>15)</sup> were isolated.



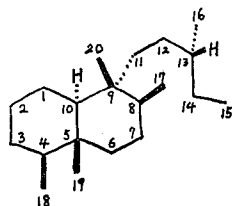
Cationic cyclizations of 33, 34, and 35 derived from manool (36) did not result in the hoped-for biogenetic-type strobane synthesis, but yielded 37, 38, and 39, respectively as well as a phyllocladane derivative 40 in the case of 35.<sup>16)</sup>

Oxidation of 34 with modified Collins reagent gave 41 (38%) and epoxyketones, 42 (17.3%) and 43 (31%), which would be useful for effecting the 1, 3-transposition of oxygen and for carrying out mixed aldol condensations. This oxidation was successfully applied to manool (36) giving rise to the higher yield of the products 44 (69%) and

45 (21%).<sup>17)</sup> Four tobacco diterpenoids 46-49 were derived from (12Z)-abienol (50).<sup>18)</sup>

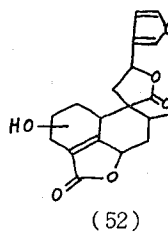
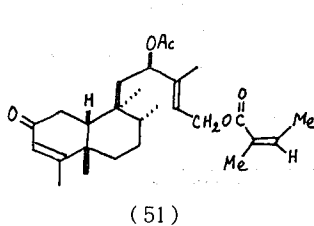


#### IV. CLERODANE DERIVATIVES

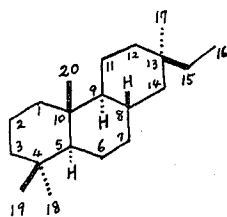


Clerodane

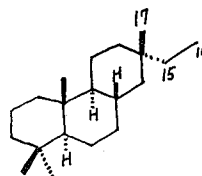
A new *cis*-clerodane-type diterpene, linarienone (51) was isolated from *Linaria japonica*.<sup>19)</sup> The structure of teucrin H1 (52) isolated from *Teucrium hyrcanicum* was determined by spectroscopic means.<sup>20)</sup>



## V. PIMARANE AND ISOPIMARANE DERIVATIVES

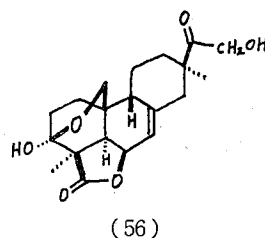
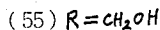
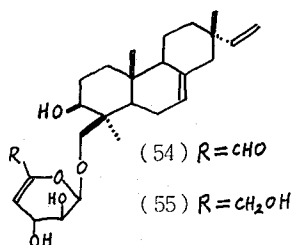
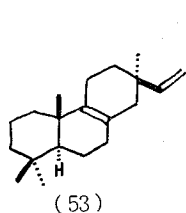


Pimarane

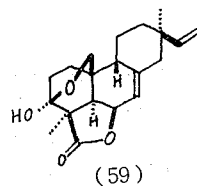
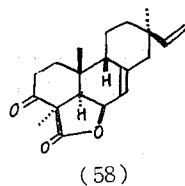
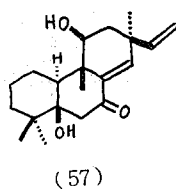


Isopimarane

Pimara-8,15-diene (53) has been isolated from *Trichothecium roseum*. Its biosynthesis is described.<sup>21)</sup> The structures of two new metabolites, virescenosides D (54) and H (55), isolated from the fungus *Acremonium Iuzulae* (Fuckel) Gams, were elucidated.<sup>22)</sup> Reinvestigation of annonalide isolated from *Annona coriacea* by X-ray analysis confirmed the stereochemistry to be as shown in 56.<sup>23)</sup>



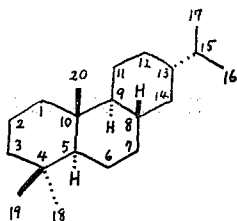
A search for growth and germination inhibitors in rice husk revealed three diterpenoids, ineketone (57), momilactones A (58) and B (59).<sup>24)</sup> The latter two were also isolated from ultraviolet-irradiated dark-grown rice coleoptiles as the major phytoalexins.<sup>25)</sup> Chemical and physical properties of momilactones A (58) and B (59) were studied in



detail.<sup>26)</sup>

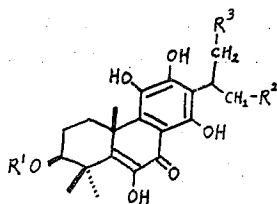
Hypocholesterolemic action of tricyclic diterpenoids in rats involving the pimarane-type has been investigated.<sup>27)</sup>

## VI. ABIETANE DERIVATIVES



Abietane

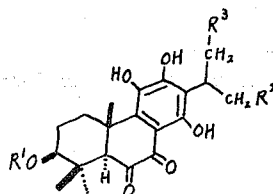
The structure of coleon L (**60**) isolated from *Coleus somaliensis* was elucidated unambiguously, which allowed to revise the structures of coleon H, I and I' to be **61**, **62**, and **63** respectively.<sup>28)</sup> The structure of coleon K was also revised to **64**, based on the fact that coleon L was easily transformed into coleon K on standing in solution.<sup>28)</sup> Coleons S (**65**) and T (**66**) were isolated from *Plectranthus caninus*.<sup>29)</sup>



(60)  $R^1 = \text{Ac}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{OAc}$

(61)  $R^1 = \text{Ac}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OH}$

(65)  $R^1 = R^2 = R^3 = \text{H}$



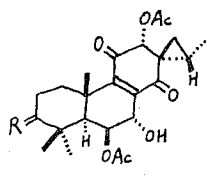
(62)  $R^1 = \text{Ac}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OH}$

(63)  $R^1 = \text{CHO}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OH}$

(64)  $R^1 = \text{Ac}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{OAc}$

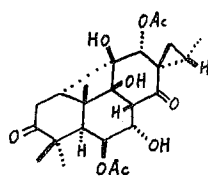
(66)  $R^1 = R^2 = R^3 = \text{H}$

The structures of three diterpenoids from *Coleus barbatus* have been determined. They are barbatusin (**67**), 3 $\beta$ -hydroxy-3-deoxybarbatusin (**68**), and cyclobutatusin (**69**). The structures of **67** and **69** were established by X-ray diffraction analysis.<sup>30)</sup> Irradiation of barbatusin (**67**) produces dehydrocyclobutatusin (**70**), whose structure was determined by X-ray methods.<sup>31)</sup>

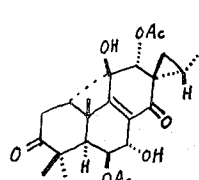


(67)  $R = \text{O}$

(68)  $R = \alpha\text{-H}$ ,  $\beta\text{-OH}$

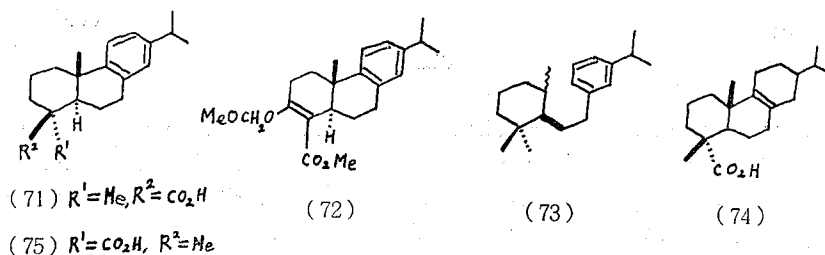


(69)

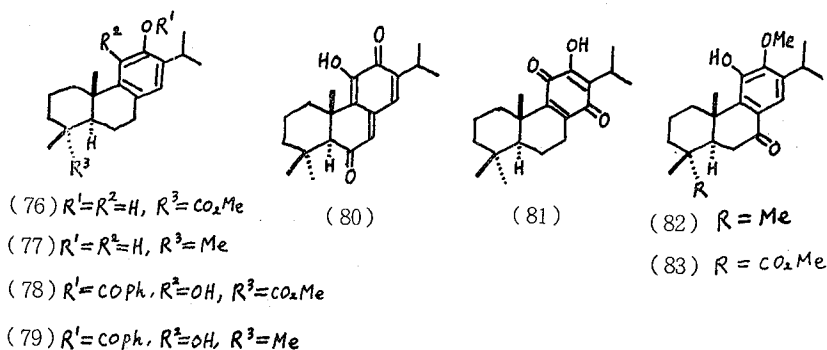


(70)

*rac*-Callitrisic acid (**71**) was synthesized through the key intermediate **72** by the same method applied to the synthesis of *rac*-podocarpic acid described in chapter II.<sup>2)</sup> Abietic acid afforded **73** on treatment with bis(2-hydroxy-1-naphthyl)disulfide at 200°, whereas toluene-3,4-dithiol at 250° gave mainly the disproportionation products **74** and **75**.<sup>32)</sup>



Oxidation at the C-11 position of methyl 12-hydroxyabieta-8,11,13-trien-18-oate (**76**) and ferruginol (**77**) were successfully carried out using benzoyl peroxide, and the resulting phenols **78** and **79** were further converted into taxodione (**80**), royleanone (**81**), cryptojaponol (**82**), and methyl 11-hydroxy-12-methoxy-7-oxoabieta-8,11,13-trien-18-oate (**83**).<sup>33)</sup>



A convenient synthesis of *rac*-ferruginol (**77**) and *rac*-sugiol (**85**) has been published.<sup>34)</sup> The outline is shown in Chart 2. *rac*-Taxodione (**80**) has been synthesized from the intermediate **84** using benzoyl peroxide oxidation as mentioned above as shown in Chart 3.

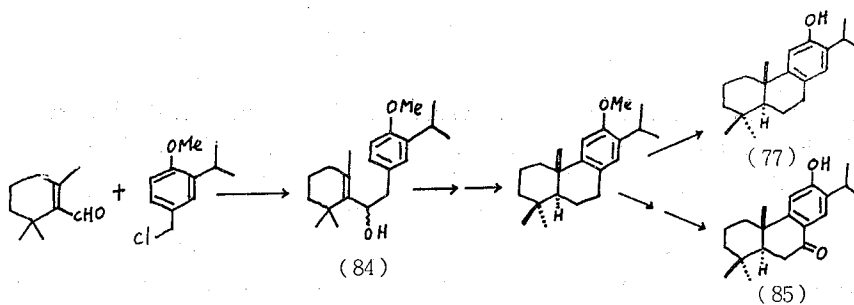


Chart 2



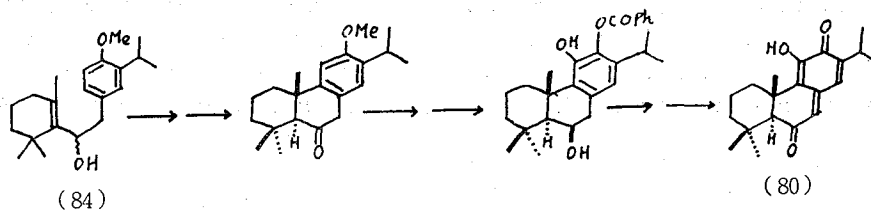
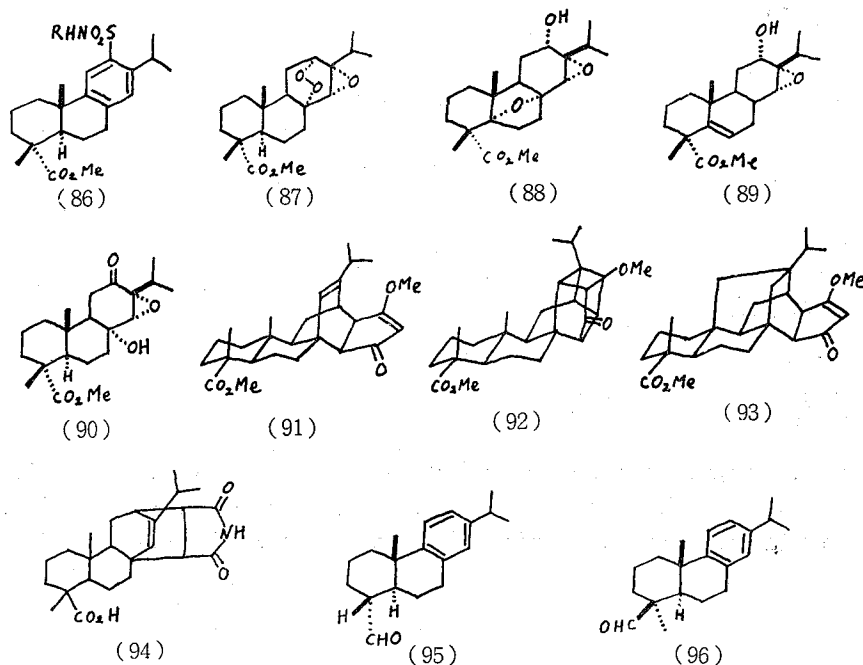


Chart 3

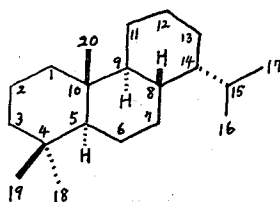
Ozonolysis of phenolic dehydroabietic acid derivatives was investigated. Direction of cleavage of the aromatic ring by means of ozonolysis was found to be affected by the substitution pattern of hydroxyl groups in the aromatic ring.<sup>35)</sup> A variety of sulfonamides **86** were obtained in 75–86% yields by amidation of the corresponding chlorosulfonyl derivatives with  $\text{RNH}_2$ .<sup>36)</sup> Epoxide **87** gave **88** and **89** on remote oxidation with ferrous sulfate.<sup>37)</sup> Compound **90** was obtained from **87** by stirring overnight with silica gel.<sup>38)</sup> The mechanism for the formation of **92** and **93** upon irradiation of **91** in benzene has been investigated by spectroscopic and by quenching and sensitization methods.<sup>39)</sup>



Imide **94** was prepared from maleopimaric acid by ammonolysis and subsequent cyclization.<sup>40)</sup> Potassium triphenylmethide was found to be effective base to prepare enolate anion. Thus, methylation of aldehyde **95** using this base and methyl iodide afforded the alkylated compound **96** in 97% yield.<sup>41)</sup>

The synthesis of (–)-podocarpic acid from (+)-dehydroabietic acid was reviewed in Japanese.<sup>5)</sup> Hypocholesterolemic action of abietane derivatives in rats has been reported.<sup>27)</sup>

## VII. TOTARANE DERIVATIVES



Totarane

Maytenoquinone (98), dispersmol (99), and dispersmone (100) were synthesized from  $\beta$ -cyclocitral (97) as shown in Chart 4.<sup>42)</sup>

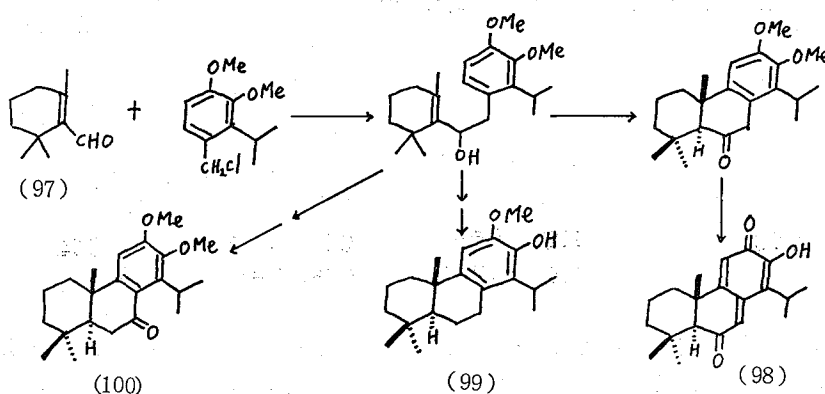
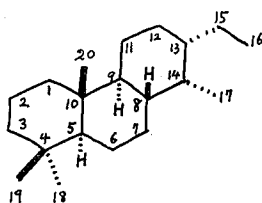


Chart 4

Hypocholesterolemic action of totarane derivatives in rats has been reported.<sup>27)</sup>

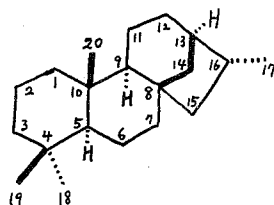
## VIII. CASSANE DERIVATIVES



Cassane

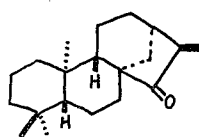
No reports were published in this period.

## IX. KAURANE DERIVATIVES

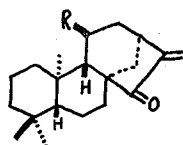
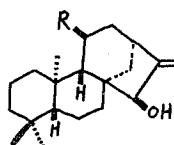
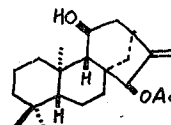


Kaurane

The isolation and structural elucidation of three *ent*-kaurane diterpenoids (101-103) from the liverwort *Jungermannia infusca* were published.<sup>43)</sup> From the liverwort *Jungermannia shaerocarpa*, *ent*-11 $\alpha$ -hydroxykauran-15 $\alpha$ -yl acetate (104), *ent*-11 $\alpha$ -hydroxykauran-15-one (105), and *ent*-kauran-11 $\alpha$ , 15 $\alpha$ -diol (106) were isolated. Their structures were confirmed by X-ray analyses.<sup>44, 45)</sup>

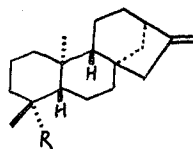
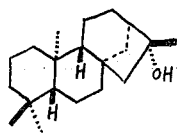


(101)

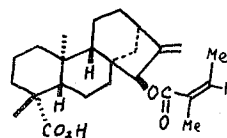
(102)  $R = H$ (105)  $R = OH$ (103)  $R = H$ (106)  $R = OH$ 

(104)

It was shown that *Austroeupatorium inulaefolium* contains three known kaurane type diterpenes (107-109) besides five new labdane type diterpenes.<sup>13)</sup> The roots of *Polymnia fruticosa* and *P. pyramidalis* were found to contain kauranic acid (107) and the derivatives 109 and 110. The aerial parts of the latter plant also contains 107.<sup>46)</sup>

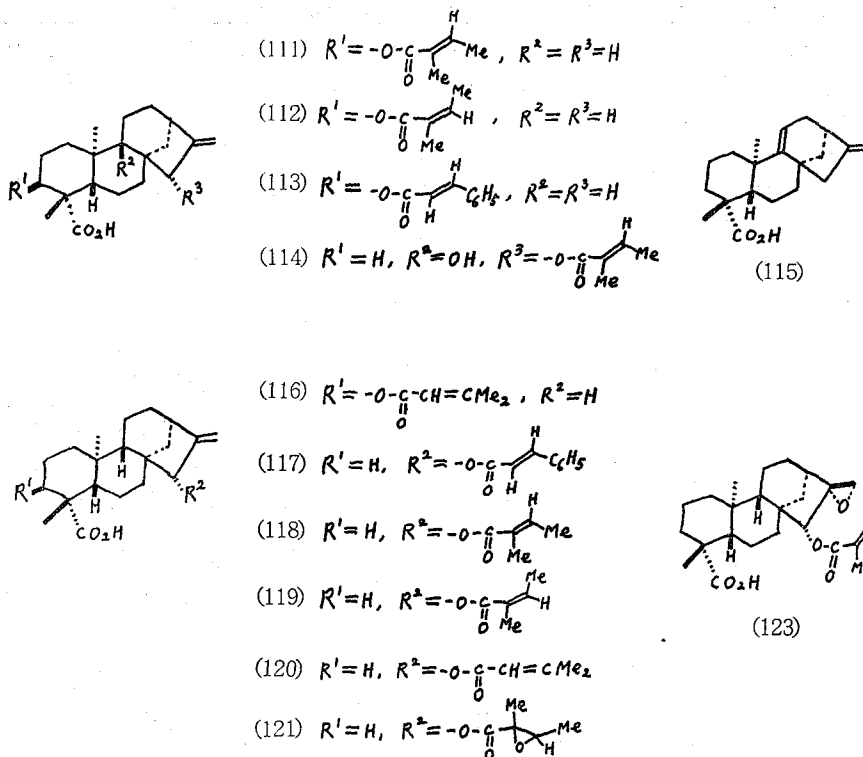
(107)  $R = CO_2H$ (109)  $R = CH_2OH$ (122)  $R = CHO$ 

(108)



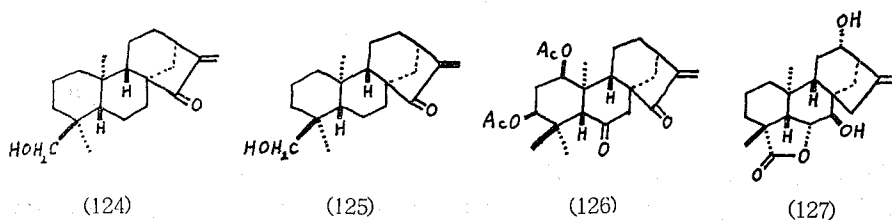
(110)

From the roots of *Wedelia triloba*, several new kauranic acid derivatives (111-114) were isolated together with the known diterpenes (107 and 115). From the aerial parts of *W. triloba*, 107, 113, 115, 116, and 117 were isolated. From the roots of *W. helianthoides*, 107, 114, 115, 118, and 119 were obtained. From the roots of *W. grandiflora*, 107, 108, 109, 114, 115, 118, 120, 121, and 122 were isolated. From the aerial parts of the same plant, 107, 109, and 115 were isolated.<sup>47)</sup>



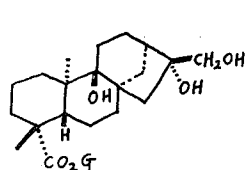
A new diterpene carboxylic acid, perymenium acid (123) was isolated from the roots of *Perymenium ecuadoricum* together with four known diterpenoids, 107, 108, 109, and 122.<sup>48)</sup>

The structures including absolute configurations of two new diterpenes isolated from *Porella densifolia* were elucidated as *ent*-18-hydroxykauren-15-one (124) and *ent*-18-hydroxykauran-15-on (125) in combination of chemical reaction and spectroscopic analysis.<sup>49)</sup> Inflexin (126) isolated from the leaves of *Isodon inflexus* was found to exhibit cytotoxicity, insect antifeedant and other bioactive properties. The structure of inflexin was determined by spectroscopic and chemical methods.<sup>50)</sup> From seeds of *Cucurbita pepo*, a new kaurenolide was isolated<sup>51)</sup> and the structure was elucidated to be 127.<sup>52)</sup>

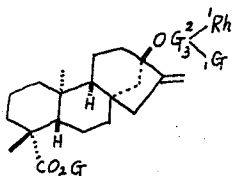


The structure of cofaryloside, a so far unknown glucoside from green coffee-beans, was determined to be *ent*- $\beta$ -D-glucopyranosyl 9 $\alpha$ , 16 $\beta$ , 17-trihydroxykauran-19-oate (128).<sup>53)</sup> From the leaves of *Stevia rebaudiana*, three new sweet glycosides, named rebaudioside-C, -D, and -E, were isolated. The structure 129 was assigned to rebaudioside-C

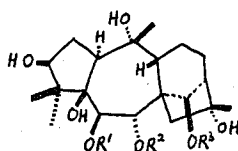
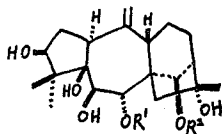
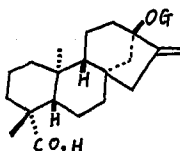
by the use of  $^{13}\text{C}$  NMR as well as chemical evidence.<sup>54)</sup> Chemical and spectroscopic examinations led to the presentation of the formulas **130**, **131**, and **132** for asebotoxin-VI, -VIII, and -IX isolated from the flowers of *Pieris japonica*, respectively.<sup>55)</sup> In the report about  $^{13}\text{C}$  chemical shifts of isoprenoid- $\beta$ -D-mannopyranosides, steviol-monoside (**133**) was described.<sup>56)</sup> The mass spectrum of  $[17-^{13}\text{C}]$  13 $\beta$ -kaur-16-ene (phyll cladene) was examined and the percentage retention of label was calculated using a computer program.<sup>57)</sup>



(128)



(129)

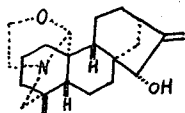
(130)  $R^1=R^3=\text{H}$ ,  $R^2=\text{COEt}$ (132)  $R^1=\text{Ac}$  or  $\text{COEt}$   
 $R^2=\text{COEt}$  or  $\text{Ac}$ 

(133)

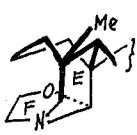
(131)  $R^1=\text{Ac}$  or  $\text{COEt}$ ,  $R^2=\text{H}$ ,  
 $R^3=\text{COEt}$  or  $\text{Ac}$  $G = \beta\text{-glucopyranosyl}$  $Rh = \alpha\text{-rhamnopyranosyl}$ 

It was found that host-plant resistance to the sunflower moth (*Homoeosoma electellum*) is caused by *ent*-kaur-16-en-19-oic acid (**107**) and trachyloban-19-oic acid.<sup>58)</sup>

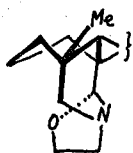
The conformational analysis of the E and F rings of atisine, veatchine (**134**), and related alkaloids was investigated. The  $^{13}\text{C}$  NMR analysis of related alkaloids did not indicate the existence of two conformers (**135** and **136**) and confirmed the existence of C-20 epimers (**137** and **138**).<sup>59)</sup>



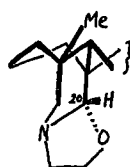
(134)



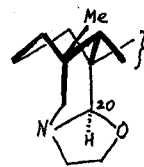
(135)



(136)



(137)

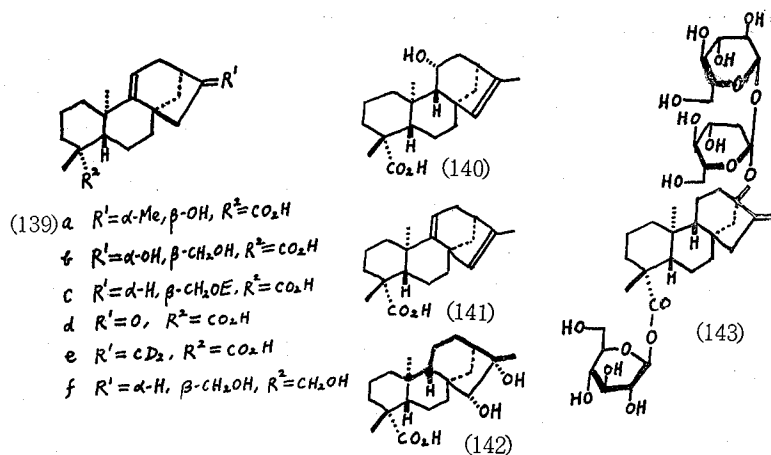


(138)

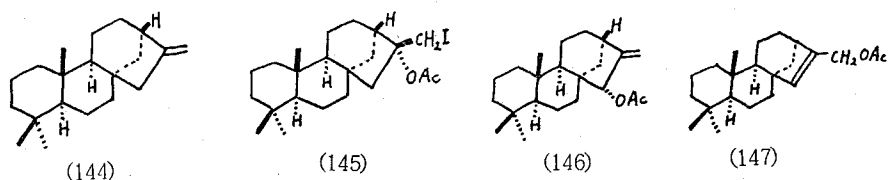
Several grandiflorencic acid derivatives **139a-f**, **140**, **141**, and **142** were prepared.<sup>60)</sup>

Acid hydrolysis of stevioside (**143**) was carried out under a mild condition with 0.4 % HCl in *aq.* methanol at reflux for 5 hours, and steviol, the genuine aglucon which had been only obtained by enzymatic hydrolysis of stevioside, was afforded in 49% yield.<sup>61)</sup> The quantitative analysis of stevioside by the application of Carr-Price reaction was examined.<sup>62)</sup>

Reactions of alkenes with thallium(I) acetate and iodine chloride were reported. In



this work 13 $\beta$ -kaur-16-ene (phyllocladene) (144) was converted to three acetates, 145 (59%), 146 (21%), and 147 (20%).<sup>63)</sup>



Treatment of *ent*-17-norkauran-16-one (148) with thallium(III) nitrate in acetic acid gave several oxidative rearrangement products, 149, 150, 151, and 152. The diterpene skeleton of those rearrangement products, *ent*-9(8 $\rightarrow$ 15 $\alpha$ H) *abeo*-kaurane (153), was synthesized as shown in Chart 5.<sup>64)</sup>

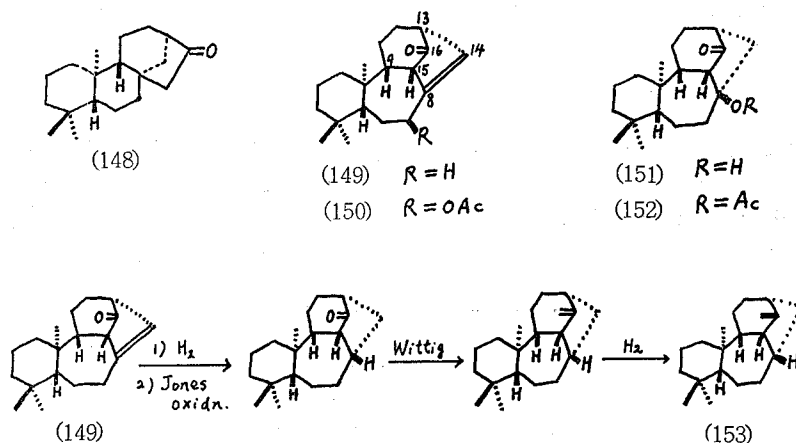


Chart 5

The stereochemistry of the photoaddition of allene to hydroindenal 154 was proved by conversion of its product 155 into steviol methyl ester (156) and isosteviol methyl

ester (157). The sequence is shown in Chart 6.<sup>65)</sup>

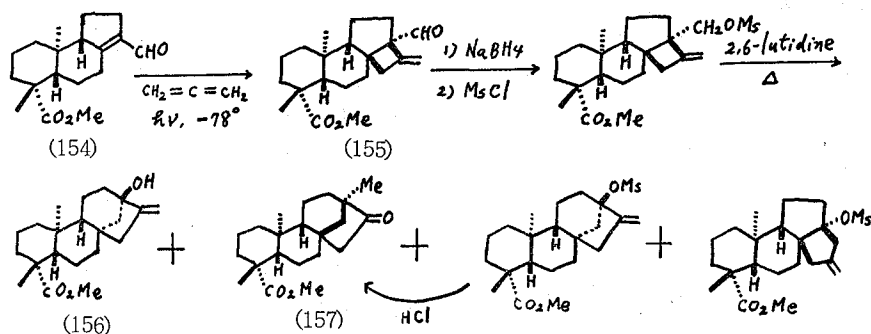


Chart 6

In experiments directed towards the total synthesis of fujenoic acid (158), the 2-(2-furyl)-6-oxobicyclo[3,2,1]octane-1-carboxylate (159) was prepared as a key intermediate. (Chart 7) Furthermore, in investigation of the model transformation into ring A of fujenoic acid, the model compound 160 was effectively converted into 161 as shown in Chart 8.<sup>66)</sup>

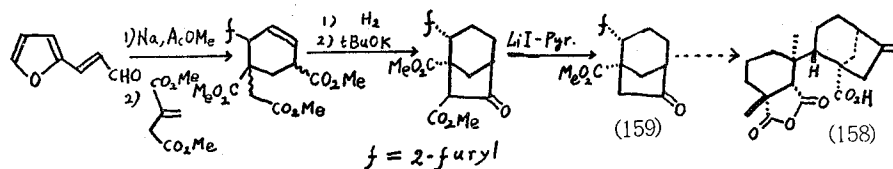


Chart 7

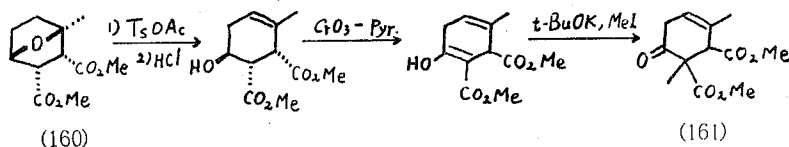
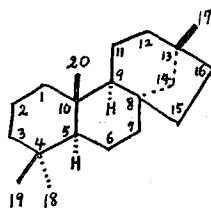


Chart 8

Total synthesis of gibberellins A<sub>15</sub> and A<sub>37</sub> using a kaurane derivative as the relay compound and chemical conversion of gibberellins A<sub>15</sub> and A<sub>37</sub> from enmein were reported.<sup>67)</sup> (See Section XI.)

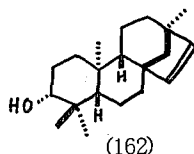
## X. BEYERANE DERIVATIVES



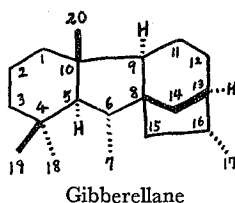
Beyerane

(124)

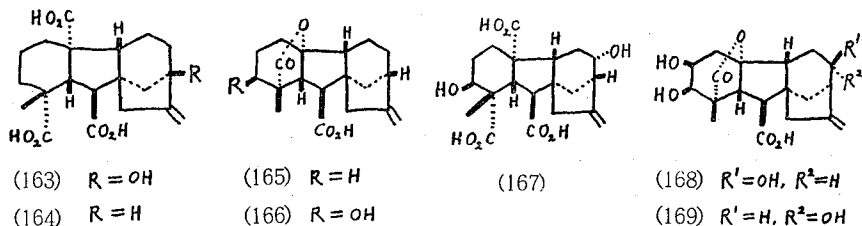
Carbon-13 NMR spectra of stachenol (162) and related derivatives were published.<sup>68)</sup> Total synthesis of isosteviol methyl ester (157) was reported.<sup>65)</sup> (See Section IX.)



## XI. GIBBERELLANE DERIVATIVES

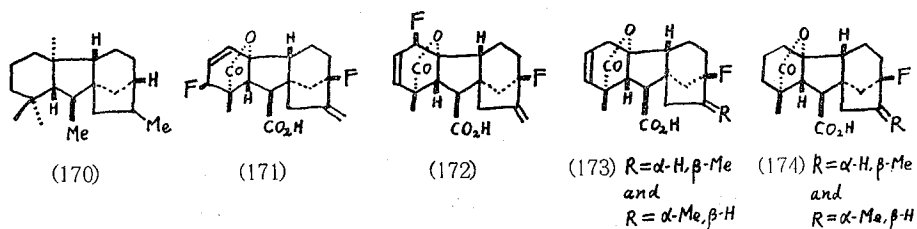


Gibberellin A<sub>17</sub> (163) was identified by GC-MS from both immature and mature seeds of *Pyrus communis*. Immature seeds also contained gibberellins A<sub>25</sub> (164) and A<sub>45</sub> (165), and two presumed mono-hydroxylated derivatives of gibberellin A<sub>45</sub>, one of which was tentatively identified as 3  $\beta$ -hydroxy-gibberellin A<sub>45</sub> (166).<sup>69)</sup> Isolation of three new gibberellins A<sub>39</sub>, A<sub>48</sub>, and A<sub>49</sub> together with a new kaurenolide was reported<sup>51)</sup> and their structures were shown to be 167, 168, 169, and 127, respectively.<sup>52)</sup>



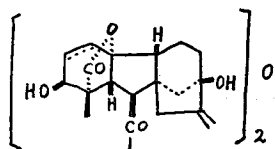
Effects of several hydrofluorene derivatives transformed from abietic acid on the growth of rice and barnyard grass seedlings were investigated.<sup>70)</sup> The negative ion mass spectra of 170 and ten C<sub>19</sub> gibberellins were discussed and compared with the positive ion mass spectra.<sup>71)</sup> Four new fluoro-gibberellins (171, 172, 173, and 174) containing bridgehead fluorine atoms were prepared by the fluorination of esters of gibberellins with 2-chloro-N, N-diethyl-1, 1, 2-trifluoroethylamine, followed by de-esterification.<sup>72)</sup>

Aminolysis of a gibberellin anhydride 175 with esters of amino acids followed by



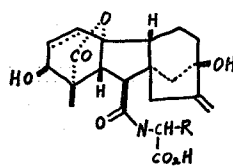


demethylation with lithium-*n*-propyl-mercaptide as well as a direct fission of the anhydride with alkali salts of amino acids led to gibberellin-aminoacid-conjugates (176).<sup>73)</sup> The O(3)- $\beta$ -D-glucopyranosides of gibberellins A<sub>1</sub>, A<sub>3</sub>, and A<sub>4</sub> (177, 178, 179) and the O(13)- $\beta$ -glucopyranosides of gibberellins A<sub>1</sub>, A<sub>3</sub>, and A<sub>5</sub> (180, 181, 182) were synthesized by means of the Koenigs-Knorr reaction. In addition to these monoglucosides the gibberellin A<sub>3</sub>-O(3, 13)-di- $\beta$ -D-glucopyranoside (183) was synthesized.<sup>74)</sup>



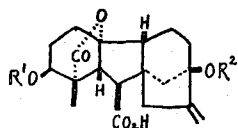
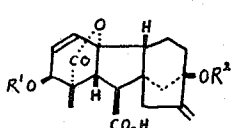
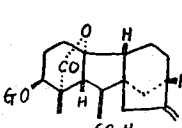
Gibberellin A<sub>3</sub>-system ( $\Delta'$ )  
Gibberellin A<sub>1</sub>-system (1,2-saturated)

(175)

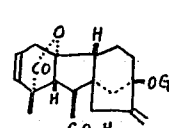


GA<sub>3</sub>-system ( $\Delta'$ )  
GA<sub>1</sub>-system (1,2-saturated)

(176)

(177) R<sup>1</sup>=G, R<sup>2</sup>=H(178) R<sup>1</sup>=G, R<sup>2</sup>=H

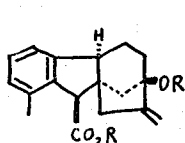
(179)



(182)

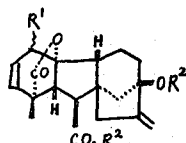
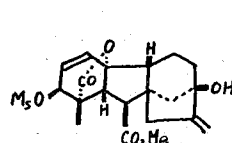
(180) R<sup>1</sup>=H, R<sup>2</sup>=G(181) R<sup>1</sup>=H, R<sup>2</sup>=G(183) R<sup>1</sup>=R<sup>2</sup>=GG =  $\beta$ -D-glucopyranosyl

The O(13)- $\beta$ -D-glucopyranoranosyl-allogibberic acid O- $\beta$ -D-glucopyranosyl ester (184) and O(13)- $\beta$ -D-glucopyranosyl ester (185) were synthesized from allogibberic acid (186) and gibberellin A<sub>5</sub> (188), respectively.<sup>75)</sup> Radioactive gibberellin A<sub>5</sub> (187) was prepared by hydrogenation of gibberellin A<sub>3</sub> derivative 189 with tritium gas followed by hydrolysis. Radioactive gibberellin A<sub>3</sub> (190) was derived from 187 by oxidation with O<sub>3</sub>O<sub>4</sub>. Radioactive gibberellin A<sub>20</sub> (191) was prepared by hydrogenation of gibberellin A<sub>3</sub>

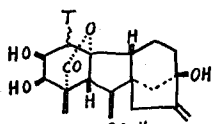
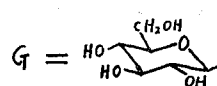


(184) R=G

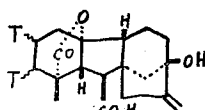
(186) R=H

(185) R<sup>1</sup>=H, R<sup>2</sup>=G(187) R<sup>1</sup>=T, R<sup>2</sup>=H(188) R<sup>1</sup>=R<sup>2</sup>=H

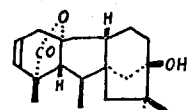
(189)



(190)



(191)



(192)

(126)

derivative **192** with tritium gas followed by removal of epoxide oxygen and hydrolysis.<sup>76)</sup>

The total synthesis of gibberellin A<sub>15</sub> (**194**) and A<sub>37</sub> (**195**) using optically active relay compound **193** which had been derived from enmein (**196**) were accomplished through a route summarized in Chart 9 and the chemical conversion of enmein into gibberellin A<sub>15</sub> and A<sub>37</sub> was also achieved through a route summarized in Chart 10.<sup>67)</sup>

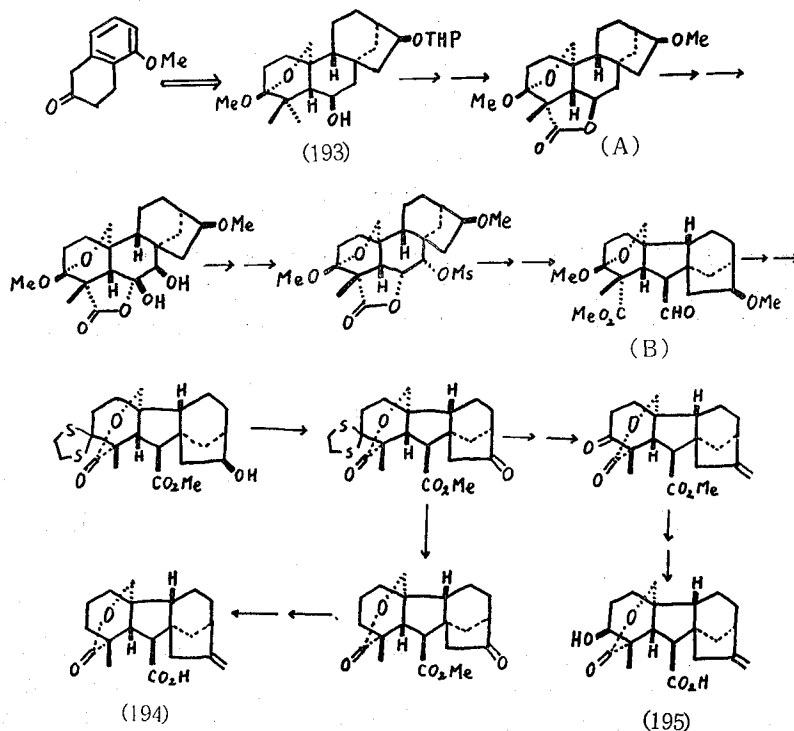


Chart 9

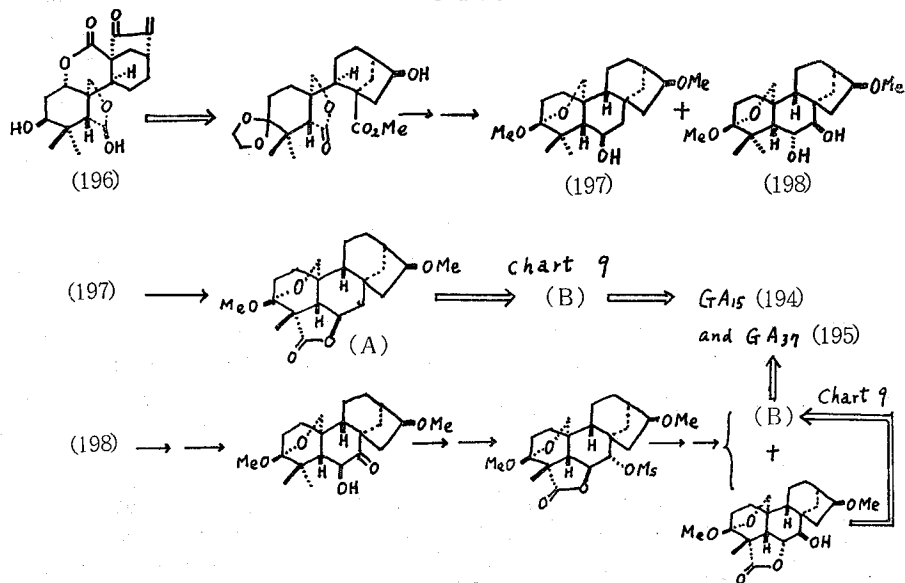
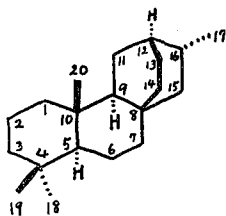


Chart 10

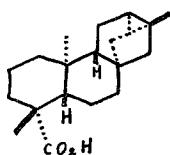
A review on the synthesis of gibberellins was published.<sup>77)</sup>

## XII. ATISANE DERIVATIVES

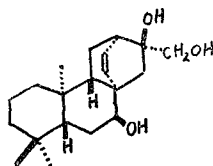


Atisane

It was found evidence that host-plant resistance to the sunflower moth (*Homoeosoma electellum*) is caused by trachyloban-19-oic acid (**199**) and kaurenoic acid (**107**).<sup>58)</sup> Isosideritol isolated from *Sideritis angustifolia* was identified as the atisenetriol (**200**).<sup>78)</sup>



(199)



(200)

It was concluded that atisine (**201**) in non-ionic solvents exists as a mixture of C-20 epimers without interconversion *via* a zwitterion of any type and in ionic solvent isomerizes slowly to isoatsine (**204**) *via* the intermediate species **202** and **203** in Chart 11.<sup>79)</sup>

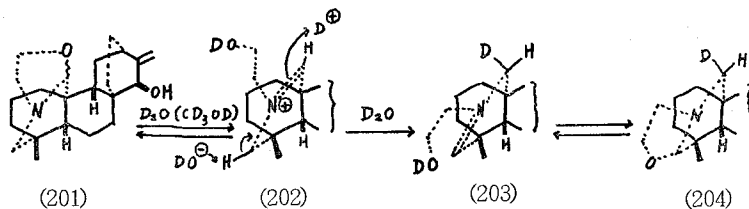
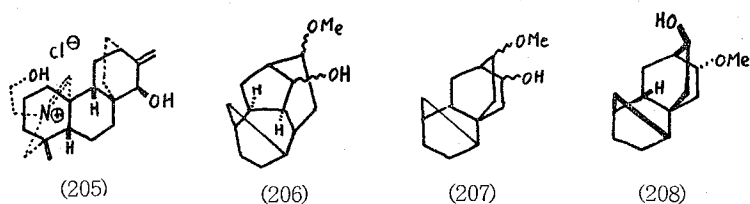
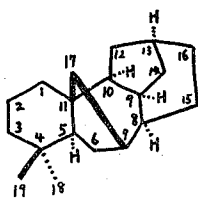


Chart 11

The <sup>13</sup>C NMR analysis of atisine (**201**) and related alkaloids confirmed the existence of C-20 epimers. Because atisine and related alkaloids are isolated as the ternary iminium salts (*e. g.* **205**) which on treatment with base generate the respective alkaloids, the question of which of the C-20 epimers of each alkaloid occurs in the plant is unanswered.<sup>59)</sup> The compound **206** was synthesized by Wiesner and his collaborators by a method that they wished to utilize in the synthesis of delphinium alkaloids. Further chemical studies, however, ascertained that the compound had failed to rearrange as predicted and **207** was then proposed. The actual structure found by the X-ray analysis was **208**.<sup>80)</sup>

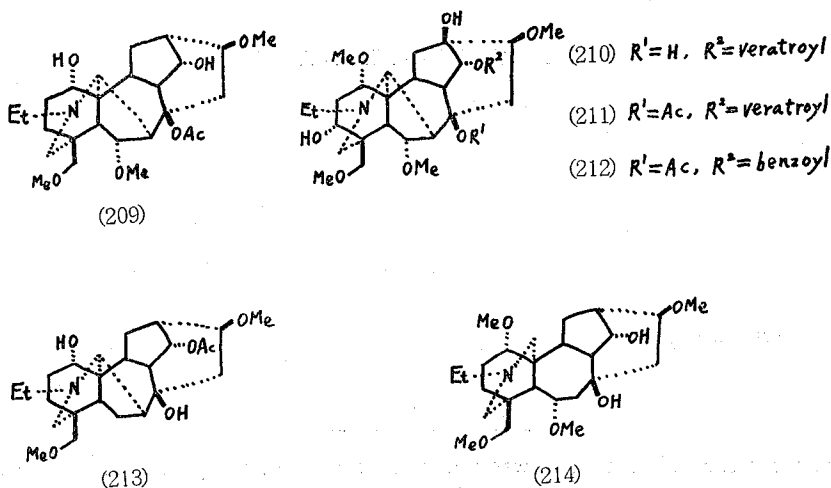


### XIII. ACONANE DERIVATIVES



Aconane

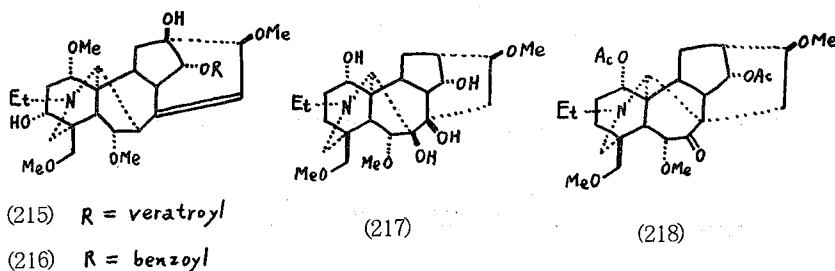
The structure of delphidine (209), a  $C_{19}$ -diterpenoid alkaloid isolated from *Delphinium staphisagria*, was elucidated.<sup>81)</sup> Three diterpene alkaloids from the roots of *Aconium falconeri* were identified as veratroypseudoaconine (210), pseudoaconitine (211), and indaconitine (212) by a successful application of  $^1H$  and  $^{13}C$  NMR spectroscopy.<sup>82)</sup> Condelphine (213) isolated from *Delphinium denudatum* was investigated by an X-ray analysis of its hydroiodide derivative.<sup>83)</sup> The crystal and molecular structure and absolute configuration of the  $14\alpha$ -benzoate hydrochloride derivative of chasmanine (214), a diterpene alkaloid of *Aconitum chasmanthum*, was reported.<sup>84)</sup>



The structures of falaconitine (215) and mithaconitine (216), two novel diterpene alkaloids isolated from *Aconitum falconeri*, were established. These are the first naturally occurring aconane alkaloids which contain a  $C(8), C(15)$  double bond.<sup>85)</sup>

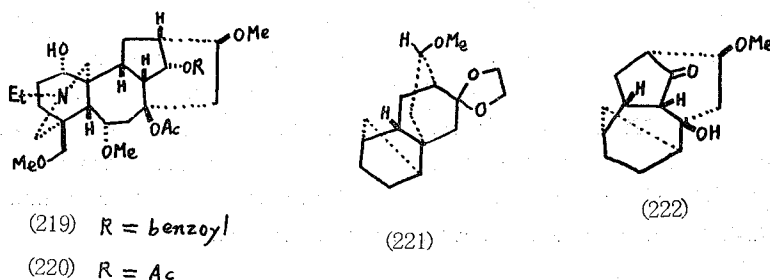
Some reactions using delcosine (lucaconine) (217), anhydrodiacetyldecosine (anhy-

drodiacetyllyucaconine) (218), and their related compounds, were reported.<sup>86)</sup>

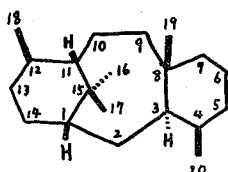


8-Acetyl-14-benzoylneoline (219) was derived from delphisine (220) *via* some steps by Pelletier *et al.* They pointed out that the suggested structure of 8-acetyl-14-benzoylneoline based on the reported data for neopelline is in error and the existence of neopelline in nature is doubtful.<sup>87)</sup>

Stereoselective syntheses of the methoxy ketal 221, which had been previously transformed to the chasmanine model compound 222, were described.<sup>88)</sup>



#### XIV. TAXANE DERIVATIVES



Taxane

No papers were published in this period.

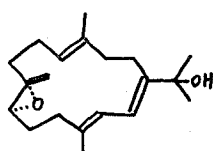
#### XV. THE OTHERS

A new cembrenoid diterpene was obtained from a *Sarcophyton* species of soft coral and its structure 223 was clarified by the spectroscopic evidence and the X-ray analysis.<sup>89)</sup>

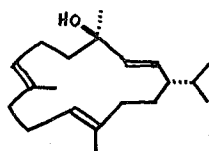
Absolute configuration of isocembrol (224) and its stereospecific synthesis from cembrene were described.<sup>90)</sup>

Asperdiol (225) was isolated from gorgonians, *Eunicea asperula* and *E. tourneforti*,

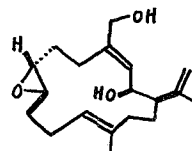
as an anticancer agent against p-388 lymphocytic leukemia *in vivo*. The structure and absolute configuration were determined by the X-ray crystallography.<sup>91)</sup>



(223)



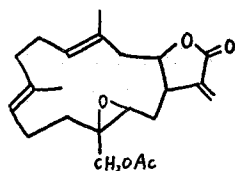
(224)



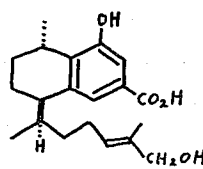
(225)

The structure **226** of lobolide, a new epoxy cembranolide from marine origin (*Lobophytum* species), was deduced on the basis of the several spectral data.<sup>92)</sup>

The structure and relative stereochemistry of dihydroxyserrulatic acid (**227**) were determined by the chemical degradation reaction and the X-ray analysis.<sup>93)</sup>



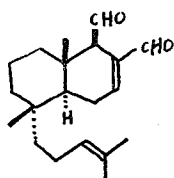
(226)



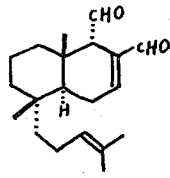
(227)

Sacculatal (**228**) and isosacculatal (**229**), two new exceptional diterpene dialdehydes, were isolated from the liverwort, *Trichocoleopsis sacculata*.<sup>94)</sup>

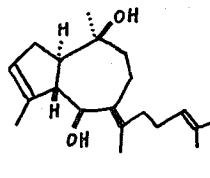
Three novel perhydroazulene type diterpenes, dictyol C, D, and E (**230-232**), were isolated from both the digestive gland of *Aplysia depilans* and algae of the family Dictyotaceae.<sup>95)</sup>



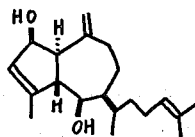
(228)



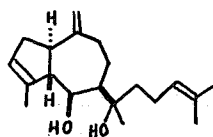
(229)



(230)



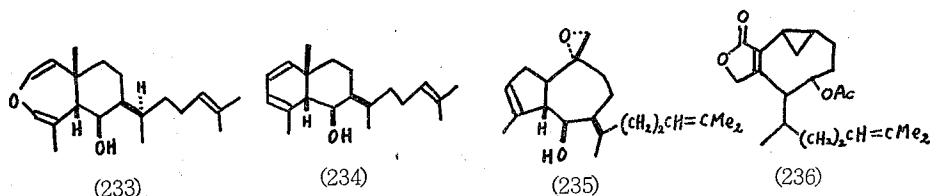
(231)



(232)

The antibiotic extracts of the marine alga *Dictyota acutiloba* were examined and two new unusual diterpenoids, dictyoxepin (**233**) and dictyolene (**234**) were isolated.<sup>96)</sup>

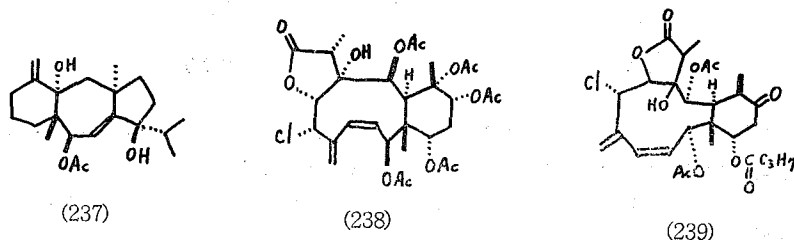
Pachydictyol A epoxide (235) was isolated from *D. flabellata* and acetoxycrenulatin (236) from *Pachydictyon coriaceum* and *D. crenulata* and their structures were determined on the basis of their spectroscopic data and chemical correlations.<sup>97)</sup>



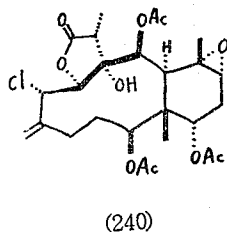
A crystal-structure analysis of 6-acetyldolatriol (237), an antineoplastic active diterpene, isolated from an Indian Ocean sea hare (*Dolabella* sp.) revealed an unusual molecular packing scheme consistent with the space group R3.<sup>98)</sup>

The X-ray analysis of briarein A (238) isolated from the gorgonian *Briareum asbestinum* was published.<sup>99)</sup>

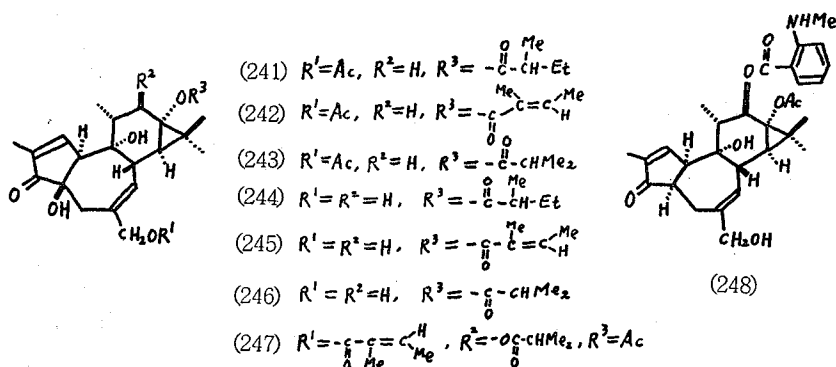
The structure of ptilosarcone, a toxic component of the sea pen *Ptilosarcus gurenegi* was suggested as shown in the formula 239,<sup>100)</sup> which was very similar to briarein A.



Stylatulide (240), the major toxic metabolite of *Stylatula* sp., was isolated. This structure was determined by X-ray analysis.<sup>101)</sup>

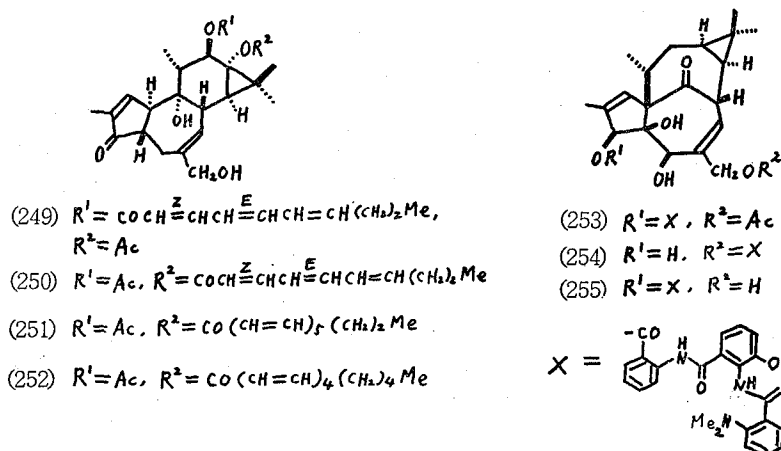


Methanol-preserved latices of *Euphorbia poisonii* and *E. unispina* were examined for irritant principles. Six 12-deoxyphorbol ester derivatives, 241-246, were identified by spectroscopic and chemical data.<sup>102)</sup> A new phorbol triester 247 was obtained from the latices of *Euphorbia frankiana* and *E. coerulescens*.<sup>103)</sup> The structure 248 of 4 $\alpha$ -sapiine, a non-irritant diterpene ester isolated from *Sapium indicum*, was reported. It is the first example of a diterpene ester alkaloid of the phorbol type.<sup>104)</sup>

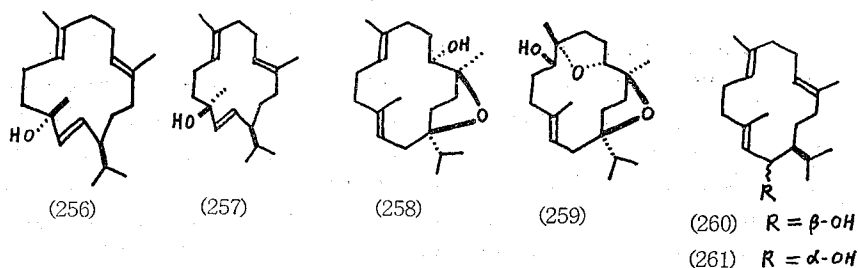


Four new highly irritant diterpenes, 249-252, were isolated from *Euphorbia tirucalli*, in addition to some inactive isomers.<sup>105)</sup> The CD spectral studies of phorbol and of some of its derivatives were published.<sup>106)</sup>

Toxic compounds were isolated from *Euphorbia Millii*. These are milliamine A (253), B (254), and C (255), the structures of which were determined from chemical and spectral evidence.<sup>107)</sup>



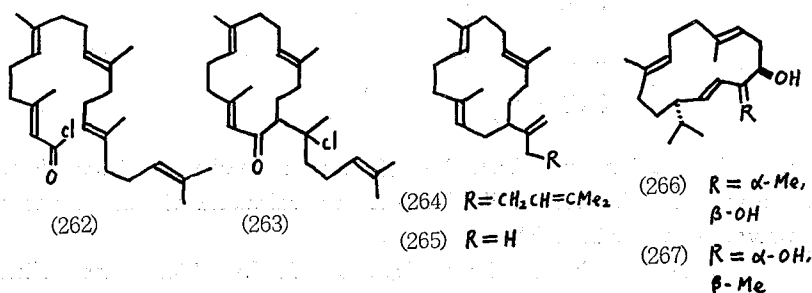
Regio- and stereo-selective synthesis of thunbergol (256) and its epimer (257) was achieved to establish the stereostructure of thunbergol which had remained unsolved.<sup>108)</sup> Likewise, in order to determine the stereochemistry of incensole (258) and isoincensole-oxide, (259), they were stereoselectively synthesized from *rac*-mukulol (260) and its epimer (262).<sup>109)</sup>



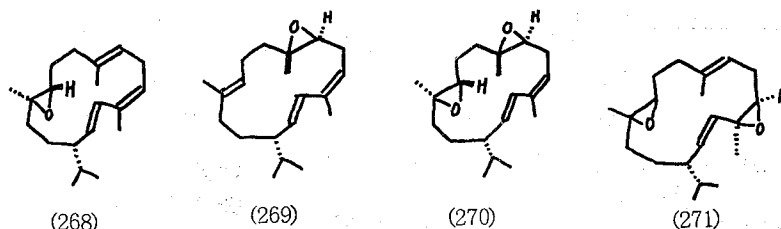


Intermolecular acylation of geranylfarnesic acid chloride (262) was successfully performed to afford albocerol skeleton 263, which was converted to 264. The compound 264, an analogue of the termite trail pheromone, neocembrene (265), showed also the pheromone activity.<sup>110)</sup>

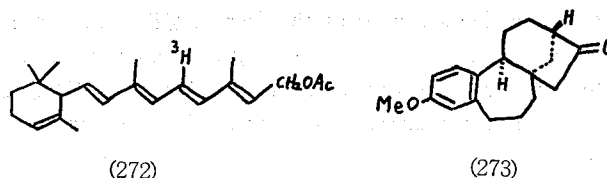
Oxidation of cembrene with  $\text{CrO}_3$  in aqueous acetone gave two epimeric cembratrienediols 266 and 267.<sup>111)</sup>



Cembrene epoxides, 268-271, were obtained by epoxidation of cembrene with peracetic acid and perbenzoic acid.<sup>112)</sup>



All *trans*- $\alpha$ -retinyl-11- $^3\text{H}$  acetate (272) was prepared in 10 steps from ethyl  $\alpha$ -ionylidene acetate and had a specific activity of 2.65 Ci/mmol and radiochemical purity  $>99\%$ .<sup>113)</sup> A stereochemically defined synthesis of compound 273 was described.<sup>114)</sup>

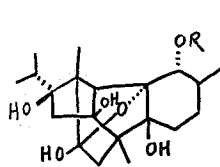
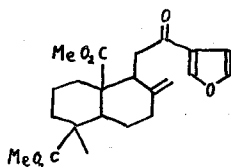


The X-ray analysis of *ent*-9(8 $\rightarrow$ 15 $\alpha$ H) *abeo*-17-norkaur-8(14)-en-16-one (149) provided a confirmation<sup>115)</sup> of the structure and stereochemistry as expected previously.<sup>64)</sup> A review article "Stereo- and regiochemistry of the Claisen rearrangement: applications to natural products synthesis" was published. Several reactions which appeared in this review must be very useful for diterpene synthesis.<sup>116)</sup>

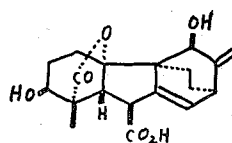
In a review on the tumor inhibitors having potential for interaction with mercapto enzymes and/or coenzymes, many diterpenes possessing unique chemical structures were

described. The creative idea and discussions in this paper may serve in the development of the new SH alkylating antitumor agents.<sup>117)</sup>

A Japanese review in relation to the insect-growth regulators from drug plants was reported, in which cinnzeylanine (274), cinnzeylanol (275), and dimethyl sciadinonate (276) were cited.<sup>118)</sup>

(274)  $R = Ac$ (275)  $R = H$ 

(276)



(277)

A review described on antheridiogen-An (277) was reported in Japanese.<sup>119)</sup> A review "The structure and synthesis of  $C_{20}$  diterpenoid alkaloids" was published.<sup>120)</sup> The  $^{13}C$  NMR of 20 tricyclic aromatic diterpenoids were reported.<sup>121)</sup> Many diterpenes were isolated from the leaves and stem bark of *Cupressus torulosa*.<sup>122)</sup> Several other papers *i. e.* "Hyptol from *Hyptis fruticosa*",<sup>123)</sup> "Doronicoside D from *Doronicum macrophyllum*",<sup>124)</sup> and "O-Acetyldelektin, a new alkaloid from *Delphinium dictyocarpum*",<sup>125)</sup> were also published.

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